Kennard & Taylor, 1983), but for bonds with O···H > 1·81 Å the mean value found is 150 (3)°, lower than the mean value 165·8 (12)° reported in the above-cited statistical study. For the N—H···O bonds the mean value of the H···O distance is 1·86 (5) Å and the mean N—H···O angle is 159 (4)°.

We thank Professor J. A. Galbis for supplying the crystals and for helpful discussions on chemical aspects and Professor A. López Castro for collecting the diffraction data. The present work is part of a project supported by a grant of the Comisión Asesora de Investigación Científica y Técnica of the Spanish Government.

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1,1′,3,3′-Tetrakis(dimethylamino)-4*H*,4′*H*-4,4′-biisoquinolyldiium Diperchlorate (II) and 1,1′,3,3′-Tetrakis(dimethylamino)-4,4′-biisoquinolyl (III)

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Abstract. (II): $C_{26}H_{34}N_6^{2+}.2ClO_4^-$, $M_r = 629{\cdot}5$, monoclinic, $I2/a$, $a = 14{\cdot}580\,(1)$, $b = 10{\cdot}760\,(1)$, $c = 18{\cdot}634\,(1)$ Å, $\beta = 90{\cdot}693\,(3)°$, $U = 2923{\cdot}1\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 2{\cdot}381$ mm^{-1}, $F(000) = 1320$, $T = 293\,(1)$ K, $R = 0{\cdot}068$ for 2606 unique reflections. (III): $C_{26}H_{32}N_6$, $M_r = 428{\cdot}6$, monoclinic, $P2_1/c$, $a = 9{\cdot}844\,(9)$, $b = 10{\cdot}580\,(9)$, $c = 24{\cdot}355\,(21)$ Å, $\beta = 109{\cdot}860\,(8)°$, $U = 2386\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}496$ mm^{-1}, $F(000) = 920$, $T = 293\,(1)$ K, $R = 0{\cdot}055$ for 4056 unique reflections. The symmetry-related halves of the cation in (II) are nearly parallel and are joined by an exceptionally long [1·597 (2) Å] bond; in the conjugate base (III) this bond is 1·496 (7) Å, the normal length for a single bond between sp^2-hybridized C atoms, and the planes of the halves of the molecule form a dihedral angle of 62·8 (3)°.

Introduction. The work reported herein arose from an investigation into the chemistry of the readily available 1,3-bis(dimethylamino)isoquinolines (I). Oxidative dimerization of (I) with aqueous silver perchlorate or cyclic voltammetry resulted in the formation

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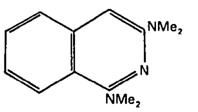
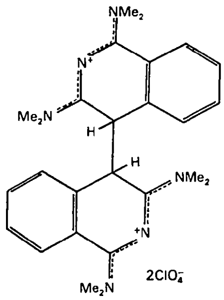
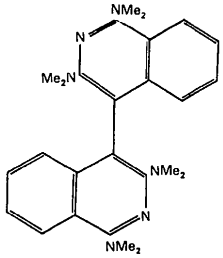
of 1,1′,3,3′-tetrakis(dimethylamino)-4*H*,4′*H*-4,4′-biisoquinolyldiium diperchlorate (II). Treatment of (II) with sodium hydroxide gave the yellow conjugate base 1,1′,3,3′-tetrakis(dimethylamino)-4,4′-biisoquinolyl (III). Details of the crystal and molecular structures are presented in the present paper; a preliminary report of the chemical details is given in Boyd, Hammerich, Lindley, Mitchell, Nicolaou & Walton (1985).



(I)



(II)



(III)

Experimental. Details of data collection and structure refinements are listed in Table 1. Space-group information and preliminary unit-cell dimensions obtained from precession photographs. Intensity data collected with a Hilger & Watts Y290 diffractometer; Ni-filtered Cu radiation; $\omega/2\theta$ step scans; moving-window estimation of intensity and background (Tickle, 1975). Reference reflections measured every 50 reflections. Lp and empirical absorption corrections (North, Phillips & Mathews, 1968) to all data.

Structures solved and refined using *SHELX*76 (Sheldrick, 1976). For (II), 35 and for (III) 16 reflections were omitted since $|F_o| << |F_c|$; the discrepancies were attributed to secondary extinction. H atoms located from difference Fourier syntheses and subsequently fixed in positions with idealized geometry and assumed C—H separations of 1·0 Å; isotropic thermal parameters for all H atoms assigned as $U = 0{\cdot}1$ Å^2. All major computations performed on the Birkbeck College VAX 11/750 or on the Amdahl computer at the University of London Computer Centre.

Table 1. *Details of data collection and structure refinement*

	(II)	(III)
(*a*) Data collection		
Crystal dimensions	0·56 × 0·37 × 0·74 mm	Fragment; max. diameter 0·55 mm
Scan step size; moving-window parameters	0·02°; 60, 40	0·02°; 60, 40
Cell parameter determination: No.; θ range of reflections	20; 20–30°	18; 20–30°
Absorption correction; max. % variation in transmission	28·9	8·7
Max. $(\sin\theta)/\lambda$ (Å^{-1})	0·601	0·601
Range *h*	−17, 17	−11, 11
k	−10, 12	−6, 12
l	0, 22	0, 28
Standard reflections: No.; variation intensity sum	4; approx. 8%	4; approx. 10%
No. of intensity measurements	4834	5746
No. of unique reflections	2606	4056
Merging *R* for equivalent *hkl*	0·010	0·013
No. of unobserved reflections $[I < 3\sigma(I)]$	142	332
(*b*) Refinement		
R	0·068	0·055
wR	0·080	0·064
Weighting scheme:	$1/\{[\sigma(F)]^2 + aF^2\}$	
a	0·0002	0·0005
$(\Delta/\sigma)_{\max}$ in final cycle	0·327	0·727
Max.; min. heights in final difference Fourier map (e Å^{-3})	0·5; −0·7	0·2; −0·2
Scattering factors	*International Tables for X-ray Crystallography* (1974)	

Discussion. Atomic parameters for non-H atoms of the two compounds are listed in Table 2.* Figs. 1(*a*) and 1(*b*) are schematic diagrams of the cation of (II) and the molecule of (III) showing the atomic labelling and bond lengths and angles with their corresponding e.s.d.'s. Figs. 2(*a*) and 2(*b*) are stereoviews of (II) and (III) respectively.

The dication (II) lies on a crystallographic twofold axis which bisects the C(4)—C(4′) bond. The two halves of the dication face one another as seen in Fig. 2(*a*) so that C(5) of one half lies above the centre of the heterocyclic ring of the other half. The dihedral angle between the planes defined by atoms C(1) to C(10) and C(1′) to C(10′) inclusive is 43·2 (1)°. The heterocyclic ring is puckered with an approximate pseudo mirror plane through C(1) and C(4), tending to increase the distance between the halves of the molecule. The phenyl ring is more closely planar; the greatest distance from its least-squares plane is 0·019 (4) Å in the case of C(9). The C(5)—C(4) [1·515 (3) Å] and C(3)—C(4) [1·508 (3) Å] bond lengths are as expected for single bonds between sp^3- and sp^2-hybridized C atoms. Elsewhere in the isoquinoline moiety the bond lengths indicate extensive electron delocalization [see formula (II)] which also includes the C(1)—N(11) [1·330 (3) Å] and C(3)—N(31) [1·321 (3) Å] regions and causes the methyl groups to lie almost in the plane of the isoquinoline moiety. The bond joining the two halves of the dication is exceptionally long [1·597 (2) Å] reflecting the potential instability of the molecule, which is stabilized only because rearrangement by transfer of the proton at C(4) to N(2) would involve an anti-aromatic and therefore forbidden transition state.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, and bond lengths and angles for the ClO_4^- anion of (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43740 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the crystal, the dications are stacked one above another forming 'tunnels' which accommodate the perchlorate anions. There are no intermolecular distances which are significantly shorter than the sums of the appropriate van der Waals radii. The C(4) atoms of the halves of the dication are related by a twofold axis and are therefore of the same chirality. However, since the space group is centrosymmetric, the structure is a racemate, containing equal amounts of D- and L-forms.

The two halves of the molecule of the base (III) are not related by crystallographic symmetry, but most equivalent bond lengths and angles agree to within two e.s.d.'s and all are within three e.s.d.'s.

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters* (Å² × 10³) *for non-H atoms*

$$U_{eq} = \tfrac{1}{3}(\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
(*a*) Compound (II)				
C(1)	0·4077 (2)	0·2804 (2)	0·3376 (1)	34 (1)
N(11)	0·4223 (2)	0·3766 (2)	0·3811 (1)	46 (1)
C(12)	0·4433 (2)	0·5038 (3)	0·3575 (2)	55 (1)
C(13)	0·4289 (4)	0·3588 (3)	0·4583 (2)	74 (2)
N(2)	0·4086 (2)	0·1682 (2)	0·3690 (1)	36 (1)
C(3)	0·4169 (2)	0·0671 (2)	0·3288 (1)	30 (1)
N(31)	0·4041 (1)	−0·0416 (2)	0·3601 (1)	35 (1)
C(32)	0·4120 (2)	−0·1618 (2)	0·3241 (2)	46 (1)
C(33)	0·3856 (2)	−0·0490 (3)	0·4376 (2)	49 (1)
C(4)	0·4453 (1)	0·0757 (2)	0·2514 (1)	27 (1)
C(5)	0·4017 (2)	0·1898 (2)	0·2178 (1)	31 (1)
C(6)	0·3755 (2)	0·1896 (3)	0·1461 (2)	41 (1)
C(7)	0·3332 (2)	0·2935 (3)	0·1168 (2)	51 (1)
C(8)	0·3153 (2)	0·3955 (3)	0·1596 (2)	52 (1)
C(9)	0·3384 (2)	0·3958 (2)	0·2313 (2)	45 (1)
C(10)	0·3848 (2)	0·2934 (2)	0·2613 (2)	33 (1)
Cl(1)	0·18557 (4)	0·32588 (7)	0·88796 (4)	47 (1)
O(11)	0·2196 (2)	0·3852 (3)	0·8253 (1)	72 (1)
O(12)	0·1039 (2)	0·3857 (3)	0·9093 (2)	74 (1)
O(13)	0·2520 (2)	0·3333 (4)	0·9433 (2)	104 (2)
O(14)	0·1677 (3)	0·2010 (3)	0·8737 (2)	116 (2)
(*b*) Compound (III)				
C(1)	0·2677 (2)	0·5807 (2)	0·2665 (1)	44 (1)
N(11)	0·1406 (2)	0·6439 (1)	0·2340 (1)	54 (1)
C(12)	0·0891 (2)	0·7416 (2)	0·2639 (1)	64 (1)
C(13)	0·0250 (2)	0·5692 (2)	0·1948 (1)	67 (1)
N(2)	0·3131 (2)	0·5924 (1)	0·3236 (1)	45 (1)
C(3)	0·4357 (2)	0·5325 (2)	0·3571 (1)	43 (1)
N(31)	0·4778 (2)	0·5594 (2)	0·4168 (1)	53 (1)
C(32)	0·3799 (2)	0·6362 (2)	0·4363 (1)	65 (1)
C(33)	0·6281 (2)	0·5927 (2)	0·4474 (1)	68 (1)
C(4)	0·5088 (2)	0·4464 (1)	0·3338 (1)	41 (1)
C(5)	0·4653 (2)	0·4399 (1)	0·2717 (1)	42 (1)
C(6)	0·5366 (2)	0·3612 (2)	0·2423 (1)	50 (1)
C(7)	0·4986 (2)	0·3637 (2)	0·1829 (1)	57 (1)
C(8)	0·3895 (2)	0·4455 (2)	0·1490 (1)	58 (1)
C(9)	0·3159 (2)	0·5185 (2)	0·1754 (1)	51 (1)
C(10)	0·3476 (2)	0·5133 (2)	0·2365 (1)	44 (1)
C(1′)	0·8215 (2)	0·2254 (1)	0·4612 (1)	41 (1)
N(11′)	0·9181 (2)	0·1644 (2)	0·5098 (1)	53 (1)
C(12′)	0·8610 (3)	0·0614 (2)	0·5342 (1)	73 (1)
C(13′)	1·0155 (3)	0·2436 (3)	0·5551 (1)	77 (1)
N(2′)	0·6833 (1)	0·2011 (1)	0·4483 (1)	42 (1)
C(3′)	0·5839 (2)	0·2619 (2)	0·4029 (1)	41 (1)
N(31′)	0·4431 (2)	0·2224 (2)	0·3914 (1)	55 (6)
C(32′)	0·3476 (2)	0·2081 (2)	0·3316 (1)	70 (1)
C(33′)	0·4096 (2)	0·1387 (2)	0·4322 (1)	70 (1)
C(4′)	0·6208 (2)	0·3595 (1)	0·3723 (1)	40 (1)
C(5′)	0·7707 (2)	0·3767 (2)	0·3819 (1)	41 (1)
C(6′)	0·8242 (2)	0·4642 (2)	0·3498 (1)	51 (1)
C(7′)	0·9684 (2)	0·4698 (2)	0·3573 (1)	59 (1)
C(8′)	1·0686 (2)	0·3900 (2)	0·3968 (1)	59 (1)
C(9′)	1·0232 (2)	0·3098 (2)	0·4307 (1)	52 (1)
C(10′)	0·8744 (2)	0·3041 (2)	0·4254 (1)	41 (1)

The two isoquinoline moieties are non-coplanar; the dihedral angle between their planes is 62·8 (3)°. The C(4)—C(4′) bond length [1·496 (7) Å] is significantly less than that of the corresponding bond in (II) and is as expected for a single bond between sp^2-hybridized C atoms. The value is in agreement with the 1·494 (3) Å found in biphenyl (Robertson, 1961), which is almost planar in the crystalline state. It therefore appears that the electron distribution in this region is not significantly affected by steric considerations.

Each isoquinoline moiety is reasonably planar; the maximum deviations from the least-squares planes defined by atoms C(1) to C(10) and C(1′) to C(10′) inclusive are 0·144 (6) and −0·156 (9) Å for C(3) and C(1′) respectively and the endocyclic bond lengths indicate extensive electron delocalization [see formula (III)]. However the C(1)—N(11) and equivalent distances [1·402 (5), 1·399 (12), 1·399 (12) and 1·382 (7) Å] are much closer to the single-bond value than in (II) and the associated methyl groups are twisted out of the plane of the isoquinoline moiety, reducing steric hindrance within the molecule.

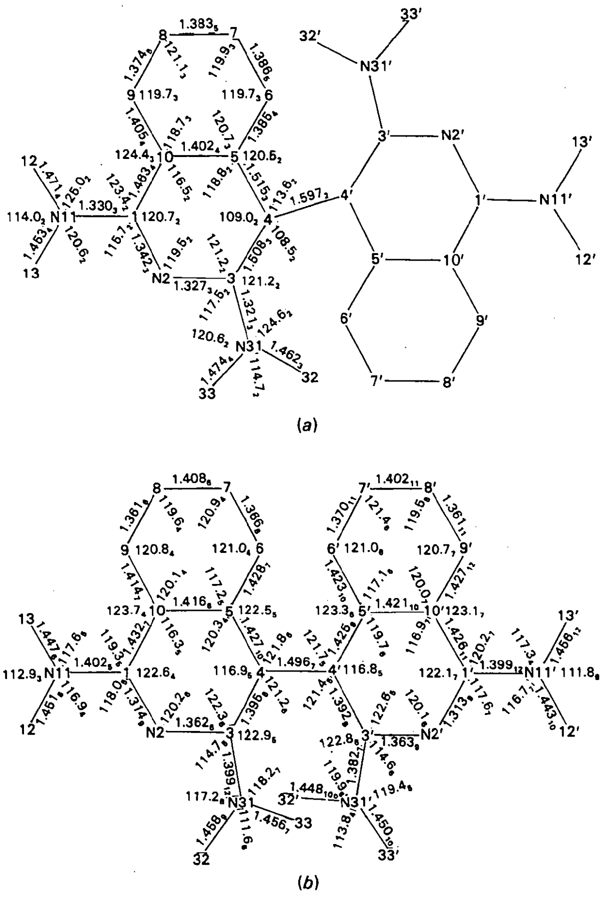

Fig. 1. Schematic diagrams of (*a*) (II) and (*b*) (III), showing the atomic numbering, bond lengths (Å) and angles (°) with e.s.d.'s given as subscripts.

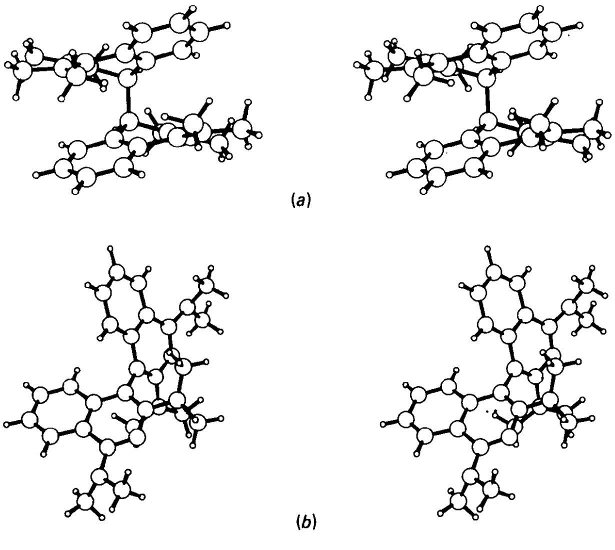

Fig. 2. (a) Stereoview of the dication of (II), viewed parallel to the b axis. (b) Stereoview of the molecule of (III).

In the crystal, some distances between methyl groups are significantly shorter than 4·0 Å which is twice the van der Waals radius for a methyl group. This is presumably achieved by inhibition of free rotation of the methyl groups.

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Structure of a Novel Oxygenated Dimer: Dilongicyclyl-12-ether*

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Abstract. Bis[(1,2,4-metheno-5,5,8a-trimethylperhydroazulen-1-yl)methyl] ether {Bis[(2,6,6-trimethyltetracyclo[5.3.1.$0^{2,7}$.$0^{10,11}$]undecyl)methyl] ether}, $C_{30}H_{46}O$, $M_r = 422\cdot7$, orthorhombic, $P2_12_12_1$, $a = 7\cdot450\,(2)$, $b = 15\cdot886\,(2)$, $c = 21\cdot466\,(2)$ Å, $V = 2540\cdot5$ Å^3, D_m(flotation in aqueous KI solution) = $1\cdot122\,(6)$, $D_x = 1\cdot105$ Mg m^{-3}, $Z = 4$, $\lambda(\mathrm{Mo}\,K\alpha) = 0\cdot7207$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 0\cdot69$ mm^{-1}, $F(000) = 936$, $T = 293$ K, $R = 0\cdot068$ for 1104 observed reflections. The oxygen atom bridges the two monomeric units, one of which has disorder in the seven-membered-ring moiety.

Introduction. While studying Lewis-acid-induced rearrangements *via* longifolene chemistry, pseudolongifolol (Mehta, Nayak & Sukh Dev, 1968) in benzene was exposed to boron trifluoride etherate; silica gel column chromatography of the resulting mixture afforded one pure crystalline compound $C_{30}H_{46}O$ (M^+ 422), in major yield (45%) (Lamture, Surayawanshi & Nayak, 1982). The structure could not easily be deduced from spectral data and X-ray analysis was required to establish this unequivocally.

Experimental. Crystal $0\cdot20 \times 0\cdot35 \times 0\cdot70$ mm; Nonius CAD-4F-11M single-crystal X-ray diffractometer; graphite-monochromated Mo $K\alpha$ radiation; $\omega/2\theta$ scan mode; scan speed 1° min^{-1}, $\theta < 23\cdot5°$, h 0 to 8, k 0 to 17, l 0 to 24, 2172 reflections collected, 1104 judged significant [$|F_o| > 3\sigma(|F_o|)$], lattice parameters from 21 reflections ($15 < 2\theta < 35°$), three standard reflections (124, 042 and 105) every 1000 s, 2% variation in intensity, no correction for absorption. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). During the final stages of refinement, it was realized that two of the atoms, C(4′) and C(5′), are disordered. A careful examination of a difference Fourier map at this stage indicated clearly the existence of these disordered atoms C(4″) and C(5″) which were refined with occupancies 0·4 and 0·5. Attempts to determine the absolute configuration of the molecule,

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